

Chemical Fingerprinting of Osprey Nest Materials following the Deepwater Horizon Oil Spill

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Abstract

The exposure of osprey to Macondo oil following the *Deepwater Horizon* oil spill was assessed through a chemical fingerprinting study of materials collected from 19 osprey nests six to seven months after the spill ended (Jan.-Feb., 2011). These samples were collected from 11 nests along the west coast of Florida southeast of Apalachicola Bay, three nests from the Pascagoula Naval Complex, Mississippi, two nests from the "interior" of the Mississippi River delta Birdfoot, Louisiana, and three nests on Horn Island located in the Gulf Islands National Seashore. The following conclusions were reached:

- Nesting material in three of the 19 osprey nests sampled contained weathered Macondo oil.
- All of these samples were collected from Horn Island in the Gulf National Seashore, the shorelines of which other studies had demonstrated were oiled from the *Deepwater Horizon* spill.
- This result demonstrates that osprey were exposed to Macondo oil. Individuals may have (a) been directly exposed to the oil and carried it into their nests, (b) carried oil-contaminated prey to their nest, and/or (c) used oil-contaminated materials to construct their nests.
- The three nests from the Pascagoula Naval Complex contained hydrocarbons derived from hydrocarbon sources other than Macondo oil.
- The two nests from the Mississippi River Birdfoot and 11 nests from western Florida did not contain Macondo oil (or any other hydrocarbon source).

Introduction

The environmental fate of crude oil released (between April 20 and July 15, 2010) from the failed Macondo well following the explosion of the *Deepwater Horizon* drill rig varied. Some fraction of the crude oil released remained within the deep ocean while a sufficiently buoyant fraction was transported (roughly) vertically ~1500 meters through the water column to the sea surface. The oil that reached the sea surface formed surface slicks, mousses, and sheens. Spread by wind and currents, some fraction of floating Macondo oil became "stranded" on shorelines across the northern GOM.

Many different types of nearshore habitats were exposed to the weathered Macondo oil along the region's barrier islands, beaches, and marshes and in the nearby shallow water sounds, bays, and bayous. Animals living within these habitats were variably exposed to the oil, including raptors, such as the osprey and bald eagle, which rely on wetland habitats.



In this study we present chemical evidence that materials collected six to seven months after the *Deepwater Horizon* oil spill ended (i.e., January-February 2011) from multiple osprey nests located on Horn Island, a barrier island located in the Gulf Islands National Seashore (Alabama), contained weathered Macondo oil. Osprey living within these nest were exposed to the oil during the collection of these nesting materials and within the nests.

Samples & Methods

Samples

Table 1 provides an inventory of the 19 osprey nest samples available for this study. These samples were collected by researchers at the Center for Conservation Biology Research at William & Mary and transferred to NewFields/Alpha Analytical, Inc. (Mansfield, MA) for analysis by the U.S. Fish and Wildlife Service. All samples were collected between January 17 and February 12, 2011 (Table 1); i.e. six to seven months after the *Deepwater Horizon* oil spill had ended (July 15, 2010). The samples consisted of various nesting materials including; twigs, seaweed, bark, grass, feathers, rope, paper, plastic and pieces of clothing. Attachment 1 provides a complete inventory of the samples analyzed and lists physical descriptions of each sample.

Figure 1 shows the locations of the 19 samples studied. As can be seen 11 of the samples were collected from nests southeast of Apalachicola Bay (Florida), three nests from the Pascagoula Naval Complex (Mississippi), two nests from the mouth of the Mississippi River delta in (Louisiana), and three nests on Horn Island located in the Gulf Islands National Seashore.

NewFields/Alpha Methods

Sample Preparation and Analytical Methods

Oiled osprey nest samples were analyzed as oily material. Oil was removed from the exterior of the nest material when visible or the exterior was rinsed with dichloromethane (DCM). The oil and rinsates were spiked with recovery surrogates and adjusted to a final volume in DCM, and passed through a filter containing glass wool and sodium sulfate. The extracts were then concentrated and cleaned using silica gel and elemental copper to remove the presence of sulfur. A 1 mL sub aliquot was then taken and spiked with internal standard for chemical analysis. The extracts were analyzed by Alpha in accordance with NOAA (2014) via:

- (1) *Saturated Hydrocarbon (SHC) Quantification and Fingerprinting:* a modified EPA Method 8015B was used to determine the amounts of TEM (C_9 - C_{44}) and individual *n*-alkanes (C_9 - C_{40}) and (C_{15} - C_{20}) acyclic isoprenoids via gas chromatography-flame ionization detection (GC/FID). Amounts of the target compounds were reported in total mg/Kg of oil weight determined gravimetrically.
- (2) *PAH, Alkylated PAH and Petroleum Biomarkers:* a modified EPA Method 8270 was used to determine the amounts of (1) approximately 80 semi-volatiles (including decalins, PAH, alkylated PAH homologues, individual PAH isomers, and sulfur-containing aromatics) and (2) approximately 50 tricyclic and pentacyclic triterpanes, regular and rearranged steranes, and triaromatic steroids via GC/MS operated in the selected ion monitoring mode (SIM). Amounts of target compounds are reported in mg/Kg of oil weight determined gravimetrically.



The analytical results for all samples analyzed by Alpha were reported through the NOAA DIVER data warehouse.

Chemical Fingerprinting Method

The chemical fingerprinting characteristics of each nest material sample were determined using oil spill fingerprinting methodology described in detail elsewhere (Stout 2015a). Briefly, this methodology involved the qualitative review of GC/FID chromatograms, GC/MS EICP chromatograms and the quantitative review of 29 diagnostic ratios (DRs) based upon measured concentrations of PAHs and petroleum biomarkers.

The nesting material samples were each classified into one of five categories, “A” through “E”, as defined in Table 2. In practice, Macondo oil was considered to be present in the samples studied that were classified as “A” or “B” (Table 2).

Results and Discussion

Overview of Chemical Fingerprinting Results

Table 3 provides a tabulated summary of the chemical fingerprinting classifications for the 19 nesting material samples studied. The results reveal:

- Three of the 19 nest materials analyzed contained weathered Macondo oil. All three of these were collected from nests on Horn Island.
- Three of the 19 nest materials analyzed contained hydrocarbons that were inconsistent with Macondo oil, i.e., hydrocarbons present were derived from a source other than Macondo oil. All three of these were collected from nest on the Pascagoula Naval Complex.
- The remaining 13 samples analyzed contained an insufficient quantity of oil to defensibly recognize the presence of Macondo (or any other) oil. These included all eleven nests sampled from the west coast of Florida and both nests sampled from the Mississippi River delta terminus in Louisiana.

Because this study was not an extensive survey involving a large number of osprey nests throughout the northern Gulf Coast, (over-) interpreting these results spatially (or statistically) is not appropriate. However, the absence of Macondo oil in all 11 nests collected from western Florida is not unexpected given they were located over 150 miles to the southeast of Apalachicola Bay, i.e., the easternmost extent of observed shoreline oiling (Fig. 1)¹. Similarly, the absence of Macondo oil in the two nest material samples collected in Mississippi River delta area may not be unexpected given that, based upon SCAT results, this *specific* area of the Birdfoot was not oiled during the spill (Fig. 2A). The analysis of the distances over which osprey may travel to gather nest materials, or over which these birds may range and encounter oil and then transfer oil to their nesting materials, is beyond the scope of this report.

The presence of Macondo oil in all three samples collected from nests on Horn Island (14047, 14045 and 906992) is not unexpected given this Island was heavily or lightly impacted by stranded oil on both the landward and seaward shorelines (Fig. 2B).¹ In

¹ Shoreline Cleanup Assessment Teams (2012) SCAT maps, available: <http://gomex.erma.noaa.gov/erma.html>



addition, chemical fingerprinting of stranded oils confirmed the presence of variably weathered Macondo oil all the way around Horn Island (Stout 2015b).

Figure 3 shows the GC/FID chromatograms obtained from the three Macondo-impacted nests on Horn Island. These each contain variably weathered Macondo oil, with the 14047 and 14045 nest samples appearing less weathered (biodegraded) oil (Fig. 3A-B) than the oil in the 906992 sample (Fig. 3C). This same range of weathering was observed among stranded oils in 2010 (Stout 2015b). Figure 4 shows the hopane-normalized PAH and petroleum biomarker histograms for the oil found in the three Horn Island nest materials. These also show the weathered character of the oil and consistency with stranded Macondo oils collected from shorelines in 2010. The somewhat reduced relative concentrations of triaromatic steroids (see yellow bars; Fig. 4) in the oil within each nest likely testify to the loss of these photo-sensitive compounds due to photo-oxidation.

The three nest material samples from the Pascagoula Naval Complex each contained hydrocarbons derived from three different non-Macondo oil sources ("E"). This area was only lightly oiled based upon SCAT results (Fig. 2B).¹ One of these (79049) contained a residual (heavy) fuel while the other two (79050 and 79022) contained hydrocarbons typical of urban background (e.g., residual oil with combustion-derived PAHs). The latter of these (79022) also containing prominent biogenic PAHs (e.g., retene) derived from plant resins (not contamination). These petroleum impacts were all chemically distinct from Macondo oil and may reflect contamination associated with the former Naval Station (closed in 2006) or other nearby source.

References

NOAA. 2014. Analytical quality assurance plan, Mississippi Canyon 252 (*Deepwater Horizon*) natural resource damage assessment, Version 4.0. May 30, 2014.

Stout, S.A., 2015a. Chemical fingerprinting methodology and the classification of oily matrices used in the Deepwater Horizon NRDA. NewFields technical report to the Trustees in support of the DARP, August 2015.

Stout, S.A., 2015b. Distribution of Macondo Oil Stranded from Supra- and Inter- Tidal Shorelines in 2010 based on Chemical Fingerprinting. NewFields technical report to the Trustees in support of the DARP, August 2015.

Table 1: Inventory of the 19 Osprey Nest Samples studied. Sample descriptions found in Attachment 1.

Client ID	Collection Date	Latitude	Longitude	State
79019	19-Jan-11	28.1606	-82.7742	FL
79040	10-Feb-11	26.8254	-82.2646	FL
79042	10-Feb-11	26.8280	-82.2716	FL
79041	10-Feb-11	26.8393	-82.2797	FL
79043	10-Feb-11	26.8323	-82.2719	FL
79037	10-Feb-11	27.1132	-82.4627	FL
79038	10-Feb-11	27.1095	-82.4500	FL
79039	10-Feb-11	27.1102	-82.4556	FL
79045	10-Feb-11	27.1316	-82.4702	FL
79046	10-Feb-11	27.1614	-82.4845	FL
79047	10-Feb-11	27.1786	-82.4938	FL
14047	17-Jan-11	30.2263	-88.6028	Gulf Isl.
14045	17-Jan-11	30.2263	-88.6060	Gulf Isl.
906992	17-Jan-11	30.2471	-88.7206	Gulf Isl.
13880	12-Feb-11	29.1335	-89.2410	LA
13879	12-Feb-11	29.1229	-89.2434	LA
79050	19-Jan-11	30.3380	-88.5701	MS
79049	19-Jan-11	30.3382	-88.5790	MS
79022	19-Jan-11	30.3330	-88.5694	MS



Table 2: Chemical fingerprinting classification of osprey nesting material samples (from Stout 2015a).

Sample's Fingerprint Classification	Description	Practical Conclusion to NRDA
A	Chromatographic features and DRs are consistent with Macondo oil or differences can unequivocally be explained by external factors*	Macondo crude oil is present
B	Chromatographic features and DRs preclude unequivocal match but differences can be reasonably explained by external factors*	
C	Not applied to oily matrices; used in the classification of sediments and tissues. Chromatographic features and DRs are equivocal but other lines of evidence support the possible presence of Macondo oil; Concentrations often low	Macondo crude oil is possibly present
D	Chromatographic features and DR are inconclusive and no other classification is justified. Most often due to a very hydrocarbon concentrations	No petroleum is obviously present
E	Chromatographic features and DRs are inconsistent with Macondo oil and cannot be explained by external factors*	Macondo oil is absent; a different petroleum is present

*For example, weathering, mixing, low(er) concentrations, and/or interferences



Table 3: Chemical fingerprinting classification results for the osprey nesting materials analyzed herein.

Client ID	Collection Date	State	Fingerprint Classification	Description
79019	19-Jan-11	FL	D	no oil present
79040	10-Feb-11	FL	D	no oil present
79042	10-Feb-11	FL	D	no oil present
79041	10-Feb-11	FL	D	no oil present
79043	10-Feb-11	FL	D	no oil present
79037	10-Feb-11	FL	D	no oil present
79038	10-Feb-11	FL	D	no oil present
79039	10-Feb-11	FL	D	no oil present
79045	10-Feb-11	FL	D	no oil present
79046	10-Feb-11	FL	D	no oil present
79047	10-Feb-11	FL	D	no oil present
14047	17-Jan-11	Gulf Isl.	A	Macondo oil present
14045	17-Jan-11	Gulf Isl.	A	Macondo oil present
906992	17-Jan-11	Gulf Isl.	B	Macondo oil present
13880	12-Feb-11	LA	D	no oil present
13879	12-Feb-11	LA	D	no oil present
79050	19-Jan-11	MS	E	non-Macondo hydrocarbons
79049	19-Jan-11	MS	E	non-Macondo hydrocarbons
79022	19-Jan-11	MS	E	non-Macondo hydrocarbons

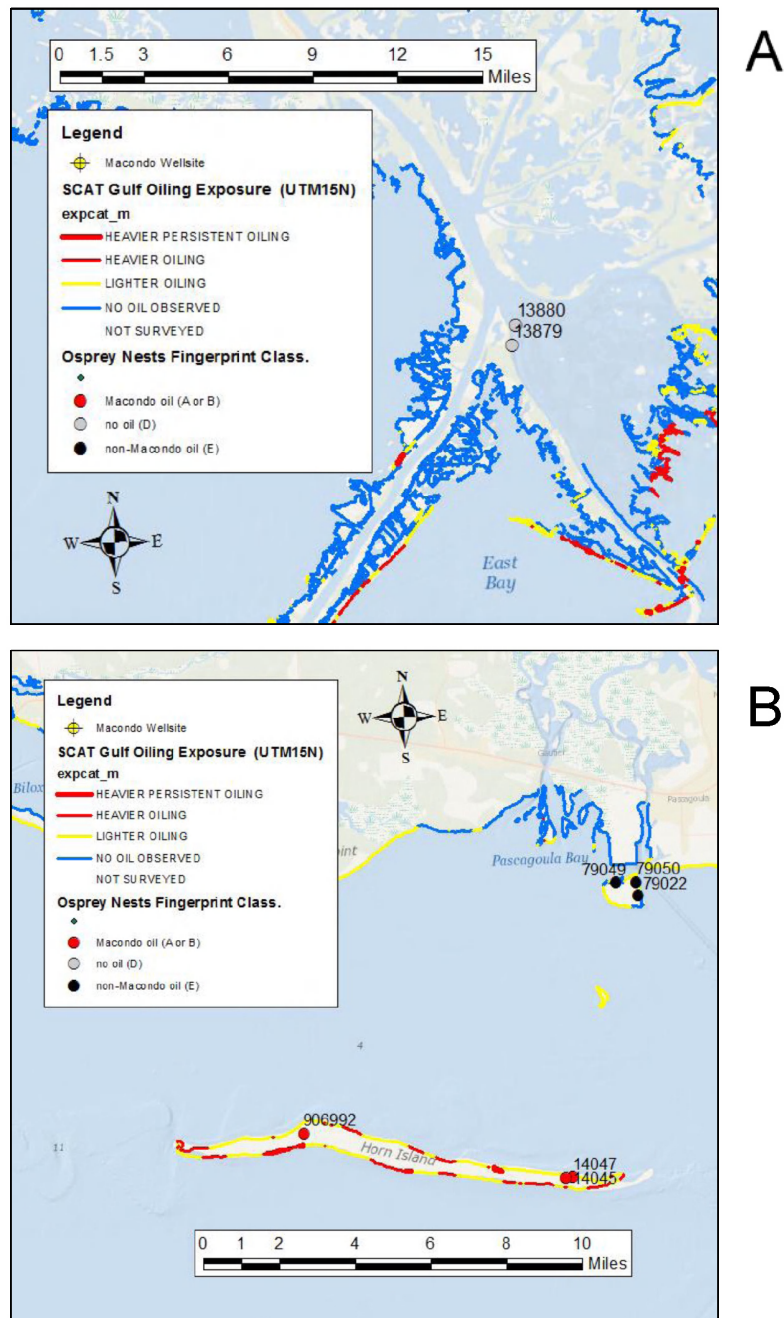


Figure 2: Map showing the chemical fingerprint classification for the osprey nest materials from (A) Mississippi River delta area and (B) Horn Island and the Pascagoula Naval Complex areas relative to SCAT maximum shoreline oiling classification.

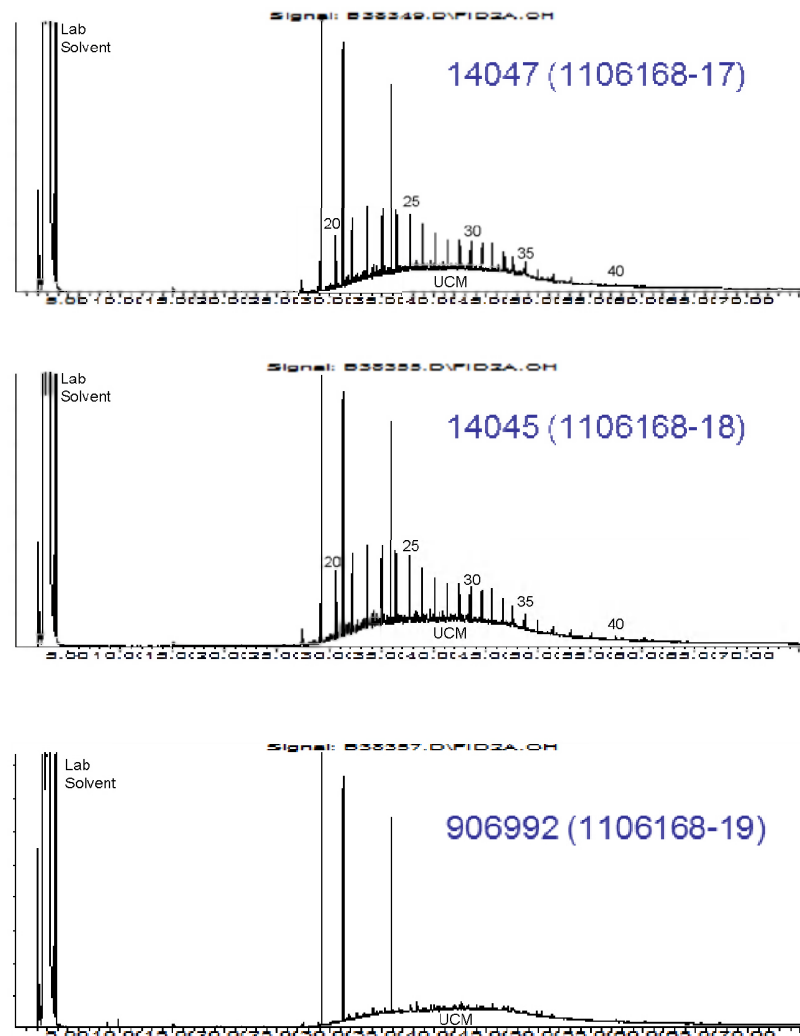
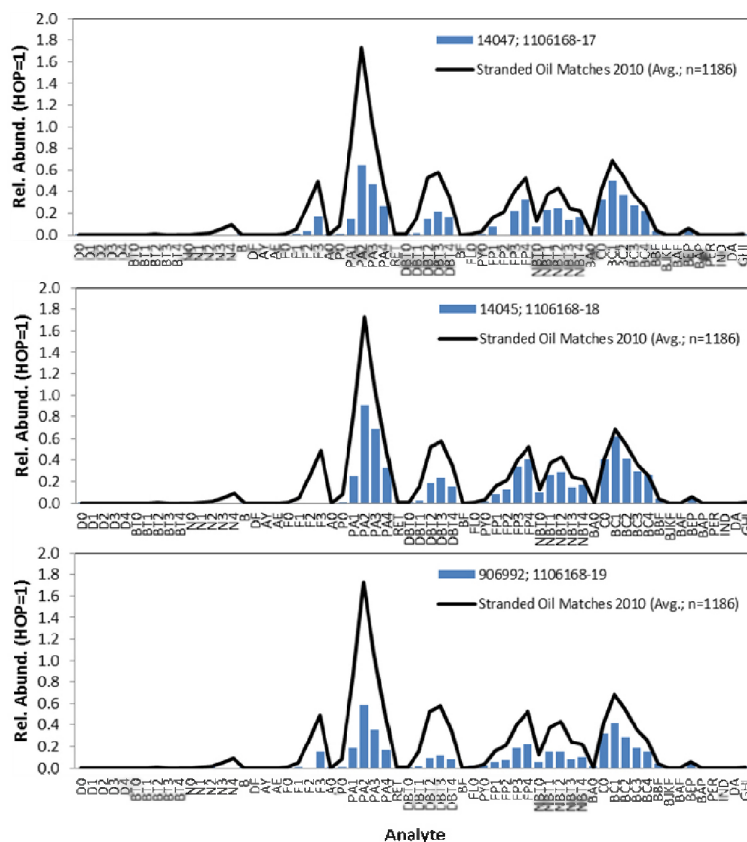


Figure 3: GC/FID chromatograms of nest materials from Horn Island containing variably weathered Macondo oil. The oil in 906992 is more biodegraded than the other oils, but still consistent with Macondo oil. The three large peaks are internal standards. # = n-alkane carbon number; UCM = unresolved complex mixture.

PAH Histograms



Biomarker Histograms

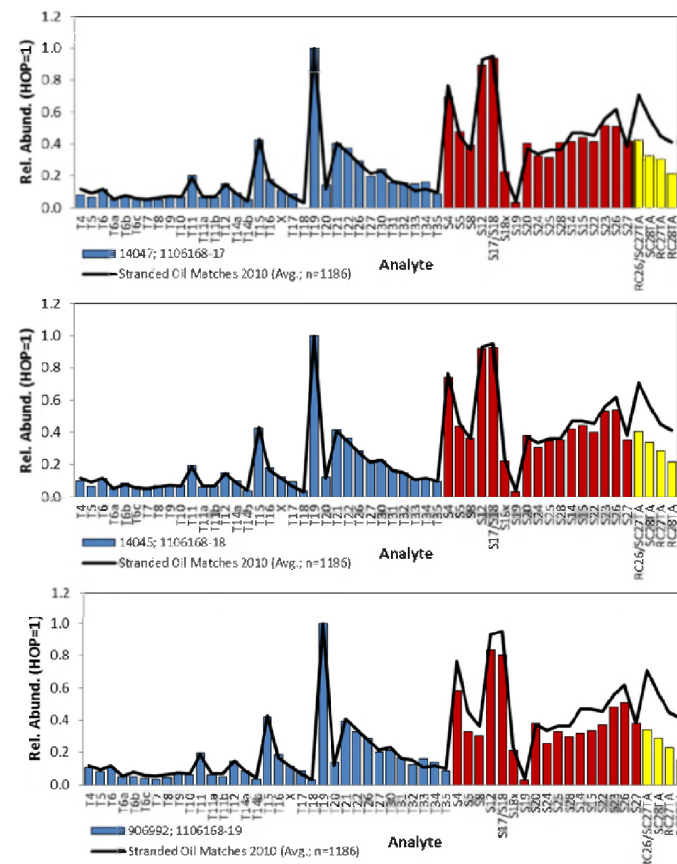


Figure 4: Hopane-normalized histograms of nest materials from Horn Island containing variably weathered Macondo oil. Histograms are compared to the average of stranded oils recovered in 2010 (Stout, 2015b). Reduced triaromatic steroids (yellow bars) is consistent with photo-oxidation of these photo-sensitive compounds. Compound abbreviations can be found in NOAA (2014).



ATTACHMENT 1

Sample descriptions made by the laboratory on the character of each osprey nest sample.

Client ID	Lab ID	Laboratory Sample Description
79040	1106168-01	Medium sized osprey nest; dark brown material, grasses and seaweed
79042	1106168-02	Small osprey nest ; dark brown + green material, pine needles and twigs
79041	1106168-03	2 bags. 1) Nest sand, leaves and grass. 2) Feathers
79043	1106168-04	2 bags. 1) Feathers. 2) nest consisting of twigs, bark and grass
79037	1106168-05	Nest seaweed, twigs, rope. Crab and clam shell
79050	1106168-06	6 bags. 1) Sticks, rope, plastic. Note plastic not rinsed. 2) lg blue cloth, sand. 3) Lg blue cloth, sand. 4) Bird feathers. 5) Bird feathers. 6) Plastic rope, pen marker, cloth. Roll of black paper
79049	1106168-07	2 bags. 1) Sticks and twigs. 2) Rope and plastic. Plastic not rinsed.
79022	1106168-08	3 bags. 1) Sand, sticks, twigs. 2) Sticks and twigs. 3) Sand, sticks, twigs
79019	1106168-09	3 bags. 1) Sticks, leaves. 2) Sticks, wood, twigs. 3) Sticks
13880	1106168-10	2 bags. 1) Reeds, moss, sticks, twigs. 2) Sm piece of cloth
13879	1106168-11	1 bag. Wood, sticks, soil
79038	1106168-12	2 bags. 1) Bird feathers. 2) Pine needles
79039	1106168-13	3 bags. 1) Pine needles, dried grass , berries. 2) Bird Feathers. 3) Bark, pine needles, twigs
79045	1106168-14	1 bag. Grass, bark, pine neeldes, sand, soil twigs
79046	1106168-15	1 bag. Pine neeldes, red and brown berries, wood, moss
79047	1106168-16	1 bag. Pine neeldes, bark, twigs
14047	1106168-17	3 bags. 1) Sticks, twigs, rope. 2) Dried grass, plastic bag. Plastic not rinsed. 3) Sticks, twigs
14045	1106168-18	4 bags. 1) Dry grass. 2) Dry grass, sand, twigs. 3) Dry grass, sand. 4) Cloth and sand
906992	1106168-19	4 bags. 1) Plastic rope, sand. 2) Wood, grass. 3) Feathers. 4) Plastic rope, grass, sand, twigs.